Porphyrins with Exocyclic Rings. 11.[1] Synthesis and Characterization of Phenanthroporphyrins, a New Class of Modified Porphyrin Chromophores

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To obtain insights into the factors that influence the electronic spectra of conjugated porphyrin systems, a series of porphyrins with fused phenanthrene subunits have been synthesized. 9-Nitrophenanthrene reacted with esters of isocyanoacetic acid in the presence of DBU in THF to give a series of phenanthro[9,10-*c*]pyrroles **14** in good to excellent yields, and subsequent acid-catalyzed condensation with various (acetoxymethyl)pyrroles **18** gave six examples of dipyrrylmethanes **17** that incorporate a fused phenanthrene ring. Cleavage of the benzyl esters from **17a** by hydrogenolysis over 10% Pd/C gave the corresponding dicarboxylic acid **24** and this condensed with diformyldipyrrylmethanes **22** under modified MacDonald "2 + 2" condensation conditions to afford the monophenanthroporphyrins **19** and **20**. Dipyrrylmethanes **17d** and **17f** with mixed benzyl and *tert*-butyl ester moieties were converted into the related formyl dipyrrylmethanecarboxylic acids **29**, and subsequent head-to-tail self-condensation in the presence of *p*-toluenesulfonic acid yielded two examples of *opp*-diphenanthroporphyrins **27**. Reaction of phenanthropyrroles **14** with dimethoxymethane and *p*-toluenesulfonic acid in acetic acid afforded the symmetrical dipyrrylmethanes **31**, and following cleavage of the ester moieties and MacDonald condensation with dialdehyde **22b**, the *adj*-diphenanthroporphyrin **30** was isolated in moderate yield. Metal chelates of the mono-, *opp*-di-, and *adj*-diphenanthroporphyrin systems were also prepared, and the electronic spectra for these modified porphyrin systems and their nickel(II), copper(II), and zinc complexes were examined. Surprisingly, the UV-vis absorptions were only slightly shifted to higher wavelengths than those for octaalkylporphyrins. Reduction of ethyl ester **14a** with lithium aluminum hydride gave an unstable carbinol, and subsequent tetramerization in the presence of BF_3 etherate and oxidation with DDQ afforded the tetraphenanthroporphyrin **10**. The free base porphyrin was virtually insoluble in organic solvents, but protonation with TFA gave a soluble dication **10**H_2^{2+} with a strong Soret band at 482 nm and two weaker absorptions at 615 and 668 nm. The bathochromic shifts for **10**H_2^{2+} are far more significant than those observed for the mono- and diphenanthroporphyrin structures, although again somewhat less than might have been expected for this extraordinarily high degree of ring fusion.

Introduction

The phthalocyanines (**1**) are among the best studied classes of organic pigments and have a myriad of industrial applications that result in the production of hundreds of successful patent applications each year.[2] They are commonly used as dyes and inks, but are also finding novel applications in the development of optical materials (photovoltaics, nonlinear optics, xerography, solar cells, optical memory and data storage, sensors, etc.), catalysts and electrical conductors.[2] Alongside the porphyrins, they also have suitable properties to act as photosensitizers in photodynamic therapy (PDT).[3] In addition, the molecular architecture of the phthalocyanines may lead to unique possibilities in molecular recognition studies and nanotechnology. In structural terms, phthalocyanines (**1**) are closely related to the porphyrins (**2**), and differ by (a) having bridging nitrogens instead of carbon linkages and (b) possessing four fused benzo units.[4] The importance of the phthalocyanines has led to the synthesis of related "conjugated macrocycles",[5] including naphthocyanines (**3**),[6] and hybrid structures such as tetrabenzoporphyrin (**4**),[7] tetraazaporphyrins (porphyrazines; **5**),[8] and macrocycles with an intermediary number of bridging nitrogen atoms.[9] The stunning array of applications for phthalocyanines and naphthocyanines in material science and elsewhere has led to the

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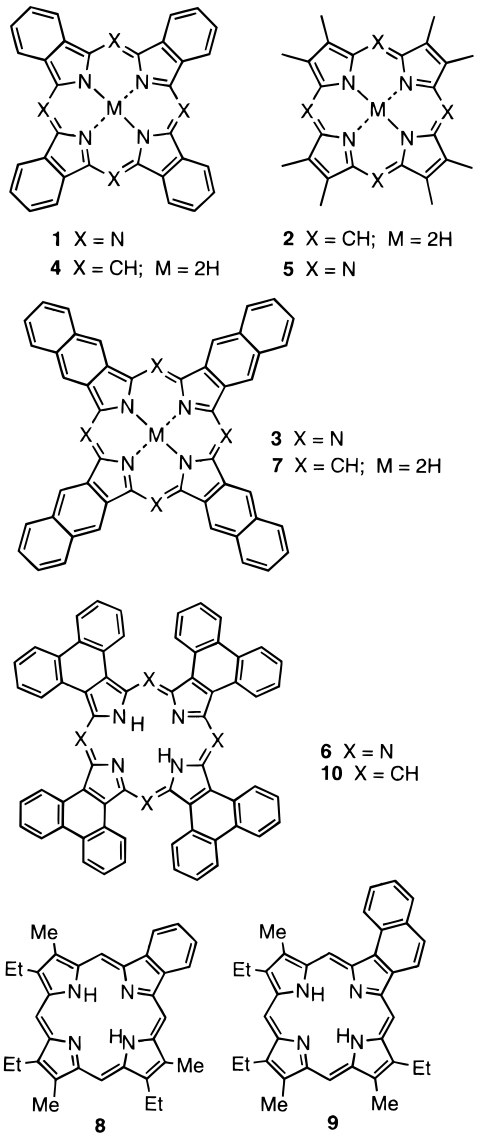
Chart 1. Conjugated Macrocycles



synthesis of more extended structures such as **6**,[10] as well as less symmetrical macrocyles.[2] However, the study of true porphyrins with fused conjugated ring systems has somewhat surprisingly received little attention, apart from investigations on tetrabenzoporphyrins.[7] Although tetranaphthoporphyrin **7** has been reported[11] and several other symmetrical systems have been noted,[12] there are presently few examples of asymmetrical porphyrins with fused aromatic rings in the literature.[13−18] In some cases, structures of this type may be generated by the modification of preformed porphyrin structures, and this approach has been applied by Crossley and co-workers to the development of so-called molecular wires.[14] We have recently synthesized benzo- (e.g. **8**)[16] and naphthoporphyrins (e.g. **9**)[17,18] of potential geochemical significance by first preparing monopyrrolic precursors bearing the required fused ring system. In extending the conjugation, it had been anticipated that the UV-vis absorption bands in naphthoporphyrin **9** would be significantly shifted to higher wavelength compared to **8**, a characteristic that would be valuable in medicinal (PDT) and material science applications. However, the observed bathochromic shifts were minor,[17] even when two naphthalene subunits were introduced.[18] In an attempt to gain further insights into the factors that influence the electronic spectra of conjugated porphyrin systems, we were interested in extending these investigations to the synthesis of porphyrins with fused phenanthrene rings (e.g. **10**).[19,20] While we were hopeful that these new systems would exhibit red shifted chromophores, the principle motivation for this work was to observe the effect of further conjugation on the porphyrin nucleus. However, these planar porphyrinoid structures might have value in other respects by virtue of their altered dimensions and geometries, and therefore could find utility in molecular recognition studies.

Results and Discussion

A prerequisite for these studies was the availability of suitably substituted phenanthropyrroles. In the synthesis of naphthoporphyrin **9**,[17a] the key dihydronaphthopyrrole intermediates were prepared by application of a Knorr-type pyrrole condensation.[21] However, this approach was not viable for the preparation of pyrroles with fused phenanthrene subunits. A valuable and popular approach to pyrrole synthesis was introduced by Barton and Zard in 1985 where readily available nitroalkenes (**11**) are condensed with isocyanoacetate esters in the presence of a nonnucleophilic base such as DBU (Scheme 1).[22−24] This involves the Michael addition of an enolate ion to the nitroalkene, followed by cyclization onto the

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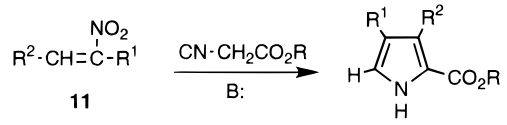
Scheme 1



isocyanate moiety and elimination of nitrous acid. Hence, the nitro group serves two functions: (1) activation of the carbon−carbon double bond toward nucleophilic attack; and (2) to facilitate the formation of the aromatic pyrrole nucleus by loss of nitrite anion. Although one would not expect this type of chemistry to occur for nitrobenzene, we speculated that 9-nitrophenanthrene might have sufficient nitroalkene character to allow the "Barton−Zard" chemistry to occur.[25−27] Nitration of phenanthrene with nitric acid−acetic anhydride leads to the formation of all five possible nitrophenanthrene isomers, but careful chromatography on alumina followed by recrystallization from ethanol affords the required isomer **12**.[28] Initially, **12** was condensed with ethyl isocyanoacetate (**13a**) in the presence of DBU in isopropyl alcohol and THF at room temperature. Condensation occurred smoothly to generate the required phenanthro[9,10-*c*]pyrrole system **14** in excellent yields, confirming our initial speculations.[25] However, a substantial amount of transesterification took place under these conditions to give a mixture of **14a** and **14b**. This transesterification must take place prior to pyrrole formation as ethyl ester **14a** does not react with 2-propanol under these conditions. Not surprisingly, if methanol is used as a cosolvent in this chemistry the methyl ester **14c** is the only product isolated. When the reaction was carried out in THF alone, the required ethyl ester was isolated in 78% yield. *tert*-Butyl isocyanoacetate (**13b**) similarly condensed with **12** to give the *tert*-butyl ester **14d** in 61−65% yield, although benzyl isocyanoacetate (**13c**)[24] afforded relatively poor yields of pyrrolic products under these conditions. This minor problem was easily overcome by reacting **12** with excess **13c** (1.2 equiv) in refluxing THF, and benzyl phenanthro[9,10-*c*]pyrrole-2-carboxylate was isolated in 87% yield after recrystallization from carbon tetrachloride.

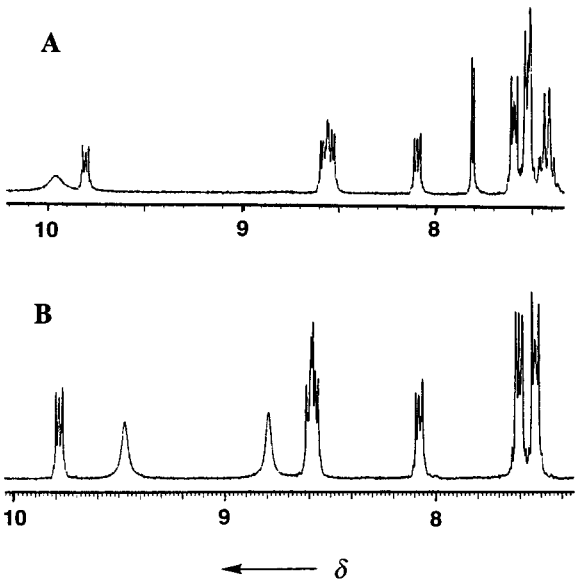
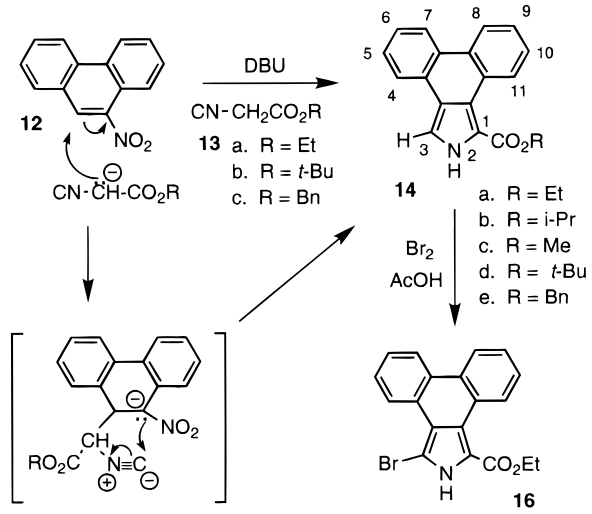


Figure 1. Partial 300 MHz proton NMR spectra of (A) phenanthropyrrole **14e** and (B) dipyrrylmethane **17c**.

Scheme 2



The proton NMR spectra for **14** were insightful, showing the majority of the phenanthrene protons between 7.5 and 8.6 ppm (Figure 1A). However, the proton overlying the carbonyl moiety at position 11 was further deshielded to 9.85 ppm by its proximity to the secondary π-system, and this observation is useful in the spectroscopic assignment of related structures. The pyrrole CH gave a doublet (J = 2.8 Hz) at 7.87 ppm, while the NH appeared as a characteristically broad resonance near 10 ppm. The EI MS for these tetracycles showed primary fragmentation by loss of ROH, and this presumably leads to the formation of the ketene radical cation **15** (Scheme 3).

The synthesis of phenanthroporphyrins could be accomplished in principle by using several different synthetic strategies, and we elected to carry out our studies by the tried and trusted MacDonald "2 + 2" condensation.[29] In any case, the construction of the porphyrin

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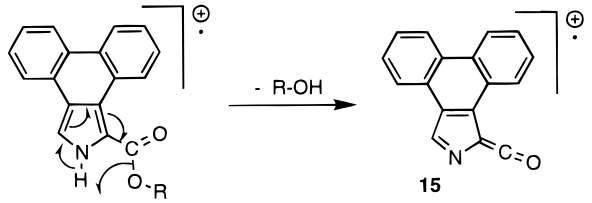
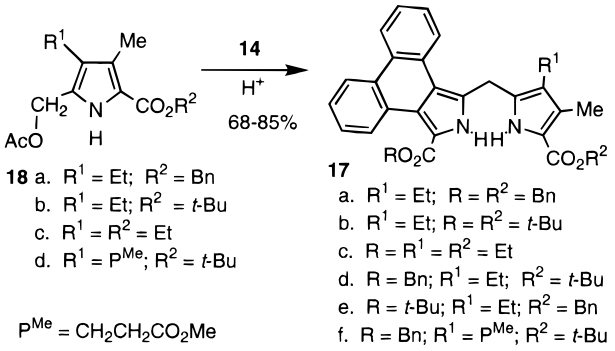
Scheme 3



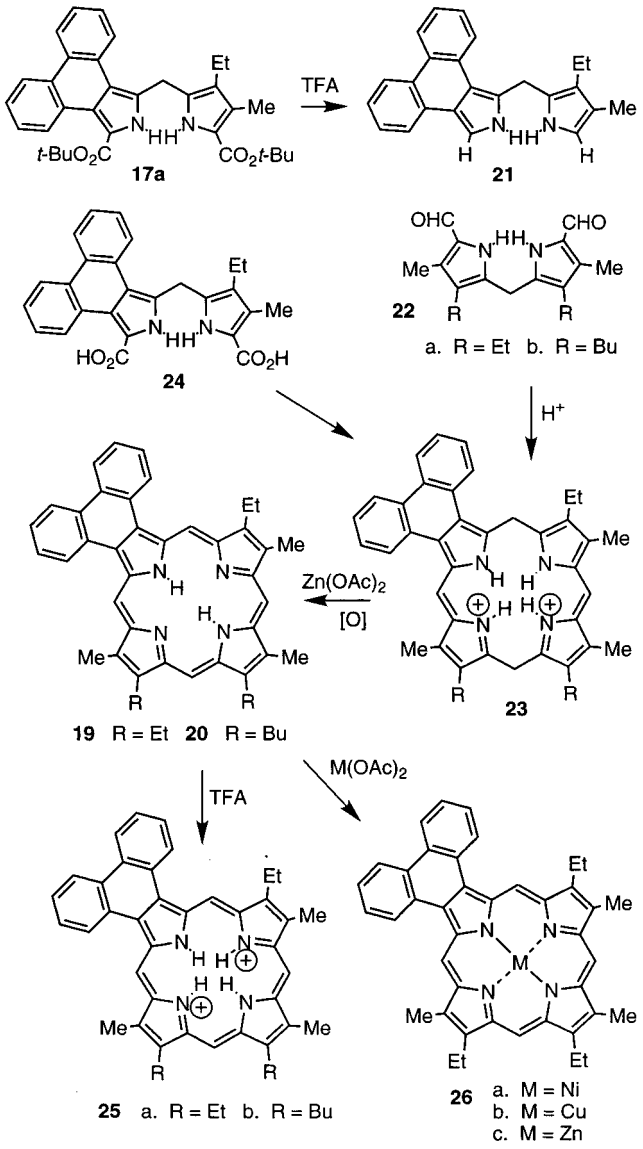
Scheme 4



macrocycle relies upon the relative propensity of the phenanthropyrrole nucleus to undergo electrophilic substitution at the α-position. While this is to be expected on theoretical grounds, this premise was initially tested by reacting **14a** with bromine in acetic acid at room temperature (Scheme 2). The corresponding α-bromo derivative **16** was generated in good yield, confirming our expectations. This chemistry was applied to the synthesis of dipyrrylmethanes **17** (Scheme 4) by condensing the well-known (acetoxymethyl)pyrroles **18** with phenanthropyrroles **14** in the presence of *p*-toluenesulfonic acid in acetic acid or Montmorillonite clay in dichloromethane.[30] The mild conditions utilized were compatible with the presence of *tert*-butyl esters, as well as ethyl and benzyl ester moieties, and six examples of the dipyrrolic system **17** were prepared in this fashion and fully characterized. These dipyrroles could be isolated as white solids, but these generally turned pink on exposure to air. However, these compounds are otherwise quite stable and further decomposition does not appear to take place even after several years. In the proton NMR spectra for **17**, the bridging methylene unit was observed at 4.5−4.6 ppm compared to values near 3.9 ppm for dipyrrylmethanes lacking the fused phenanthrene moiety. This downfield shift is consistent with the deshielding anisotropy of the proximal polycyclic π-system (Figure 1B).

Monophenanthroporphyrins **19** and **20** were prepared using the MacDonald "2 + 2" synthesis from dipyrrylmethanes **17a** and **17b** (Scheme 5). The bis-*tert*-butyl ester **17a** was treated with TFA at room temperature for 15 min, and the resulting mixture diluted with dichloromethane, washed with aqueous sodium bicarbonate solution, dried, and evaporated to give the deprotected diunsubstituted dipyrrylmethane **21**. Condensation with diformyldipyrrylmethane **22a** in the presence of *p*-toluenesulfonic acid in methanol−dichloromethane, followed by addition of zinc acetate and air oxidation of the porphodimethene intermediate **23**, afforded the extended porphyrin structure **19** in modest yields. The low yields

Scheme 5



(12%) obtained in this chemistry were disappointing, but we felt that this might have been due to the instability of the diunsubstituted dipyrrylmethane **21** and the extensive handling required to isolate this intermediary species. To overcome this perceived problem, the related dicarboxylic acid **24** was prepared by hydrogenolysis of the dibenzyl ester **17b** over 10% palladium−charcoal. The dicarboxylic acid would be expected to undergo in situ decarboxylation to generate **21** under the conditions utilized to carry out the porphyrin condensation. In the event, reaction of **24** with dialdehyde **22a** afforded phenanthro[9,10-*b*]porphyrin **19** in 29% yield. Reaction of **24** with the dibutyldipyrrole **22b** similarly gave porphyrin **20**, although the yield was only 18% in this case. However, this was raised to over 30% yield when more dilute conditions were used for the "2 + 2" condensation.

The structures of **19** and **20** were confirmed by NMR spectroscopy and mass spectrometry. The proton NMR spectra were consistent with the expected aromatic structures and exhibited the usual powerful porphyrin diatropic ring current. For instance, the methyl substituents were shifted downfield to 3.5−3.6 ppm, values that are in the typical range for β-alkyl-substituted porphy-

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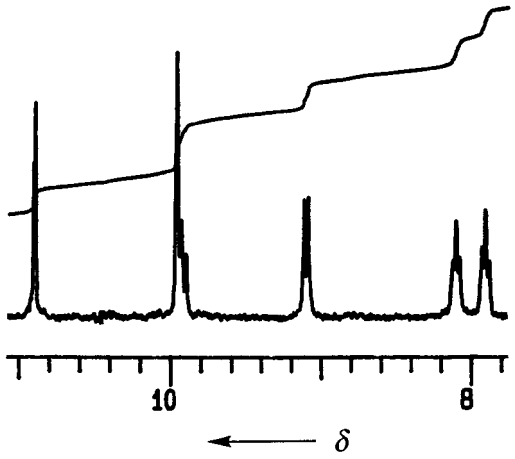


Figure 2. Partial 300 MHz NMR spectrum of phenanthroporphyrin **19**.

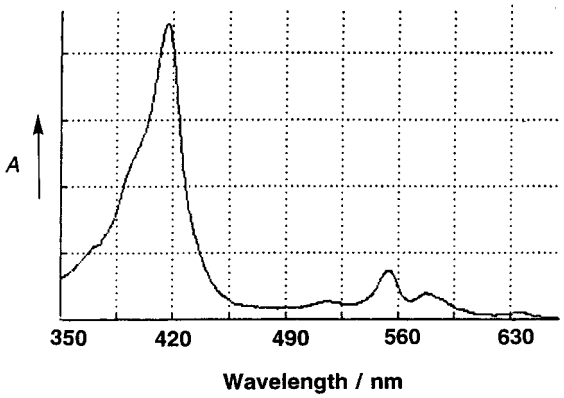
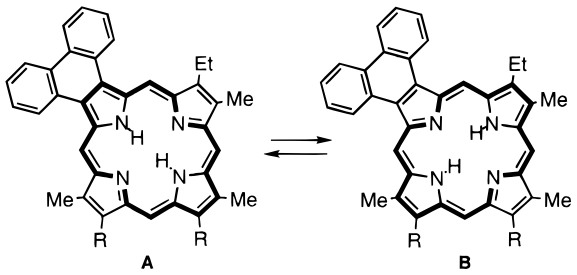


Figure 3. UV−vis spectrum of phenanthroporphyrin **19** in dichloromethane.

rins. In addition, the internal NHs resonated at a typical value of −4.0 ppm, while the external *meso*-protons appeared near 9.8 (for 2H) and 10.74 (for 2H) ppm (Figure 2). The downfield 2H resonance corresponded to the *meso*-protons adjacent to the phenanthrene subunit, and the additional deshielding is undoubtedly due in part to the proximity of these methine protons to the phenanthrene π-system, although steric interactions may also be a factor. By the same token, the two phenanthrene protons nearest to the porphyrin macrocycle were considerably deshielded and were observed near 9.8−9.9 ppm. The UV-vis spectra for **19** and **20** closely resembled the spectra obtained for naphtho[1,2-*b*]porphyrin **9**, and the bathochromic shifts for the major λ_{max} values were all less than 4 nm (Figure 3). For **19** and **20**, a strong Soret band appeared at 417 nm, compared to 415 nm for **9**, and the Q-band region was unexceptional. The most red shifted band (Q_1) was relatively weak and appeared at 634 nm, compared to a value of 630 nm in the naphthoporphyrin case. These results suggest that the porphyrin chromophore virtually ignores the presence of the phenanthrene ring system and the π-interactions clearly do not follow the simplistic trends that we had originally anticipated. In the presence of TFA, dications **25** were generated and these showed split Soret band at 403 and 420 nm. This spectrum differs considerably from the spectra for octaalkylporphyrin dications, which exhibit a single Soret absorption. One factor that is difficult to assess in these studies is that phenanthroporphyrins **19** and **20** most likely exist as two rapidly interconverting

Scheme 6



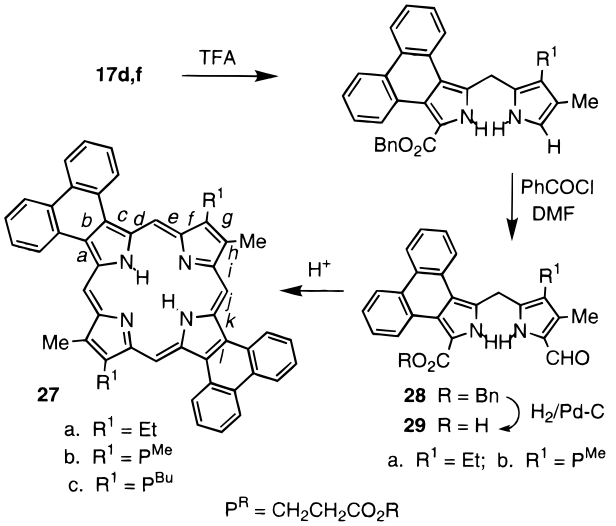
tautomers (Scheme 6). These structures represent different chromophores and may have quite distinct absorption spectra. The observed UV-vis data, according to the Franck−Condon principle, will correspond to a superimposition of the two sets of absorptions, although it is certainly possible that one tautomer will predominate. In tautomer B, the 18 π electron delocalization pathway within the porphyrin macrocycle bypasses the phenanthrene nucleus altogether, and the dominance of this species might explain the limited shifts observed. For the free bases of these porphyrins, the phenanthrene unit behaves more like an auxochrome than part of a truly conjugated system, and these considerations may allow the data to be rationalized. In the dication, tautomerization is no longer a factor, and the phenanthrene subunit may exert a larger effect in this case. However, the crowded macrocyclic cavity is likely to induce the system to attain a less planar conformation, and this may also be a factor.

To further investigate this phenomenon, the corresponding nickel(II), copper(II), and zinc complexes (**26a**−**c**) were prepared. These all showed single Soret bands at 412, 414, and 418 nm, respectively. The longer wavelength region was two-banded, as is typically observed for metalloporphyrins, where the higher wavelenth or α-band was more intense than the lower wavelength β-band. The relative intensity of the β absorption increased from Ni to Zn, and both bands underwent bathochromic shifts with increasing atomic number for the coordinating transition metal cation. All of these trends are seen for simple octaalkylporphyrin chelates such as for octaethylporphyrin (OEP).[31] The red-shifting influence of the phenanthrene subunit on the λ_{max} values for these metal complexes were on the order of 11−27 nm compared to the OEP chelates. The relatively small shifts involved are comparible for the free base porphyrins (**19** vs OEP), and this demonstrates that the electronic structure of the metal chelates is similar to the parent structures. No tautomeric processes can be operating for **26a**−**c** and it remains unclear why the π-system of the phenanthrene exerts such a small effect. Further speculation will have to await detailed theoretical analyses.

Although the phenanthroporphyrin chromophore in **19** or **20** showed no unusual electronic absorption properties, the synthesis of diphenanthrene appended structures was considered to be a worthwhile goal. In addition to discovering more about the electronic properties of porphyrins with fused aromatic rings, the well-defined nature of these extended porphyrin structures may have relevence to the development of nanomolecular based

(31) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed., Elsevier: New York, 1975; pp 871−889.

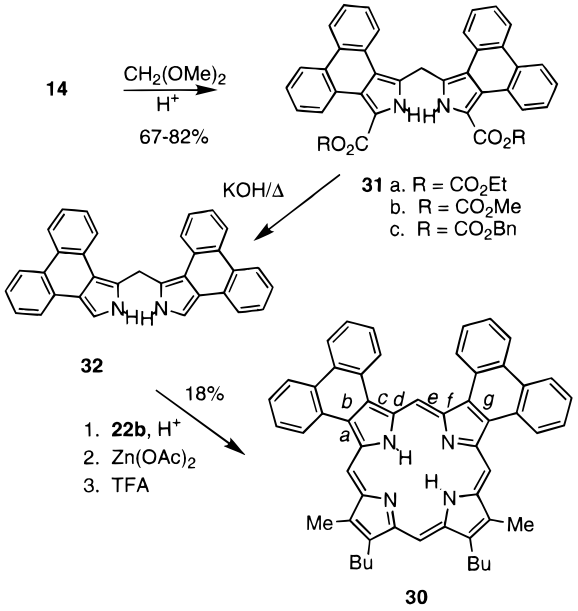
Scheme 7



systems such as molecular wires.[14] The successful synthesis of **19** and **20** using the MacDonald condensation suggested that the same strategy could be utilized in the synthesis of diphenanthroporphyrins. The *opp*-diphenanthroporphyrin system **27** can be prepared by the self-condensation of a suitably substituted dipyrrylmethane monoaldehyde (Scheme 7). The mixed ester dipyrroles **17d** and **17f** were treated with trifluoroacetic acid to cleave the *tert*-butyl ester protective groups and subsequent formylation with Clezy's variant on the Vilsmeier reaction (PhCOCl−DMF)[32] gave the corresponding aldehydes **28**. Hydrogenolysis over 10% palladium on activated carbon then gave the related carboxylic acids **29**. Formyldipyrrylmethane **29a** was treated with *p*-toluenesulfonic acid in methanol−dichloromethane and this induced the decarboxylation of the pyrrolecarboxylic acid, followed by a head-to-tail self-condensation of two dipyrrolic units. Following addition of zinc acetate, air oxidation, and workup, the required porphyrin **27a** with two oppositely fused fused phenanthrene rings was isolated in good yields. Unfortunately, this compound was very difficult to work with due to its virtual insolubility in most organic solvents. Self-condensation of **29b** gave the related *opp*-diphenanthroporphyrin **27b**, and this compound was slightly more soluble in chloroform giving green solutions. Transesterification with *n*-butyl alcohol gave the corresponding dibutyl ester **27c**, and the longer side chains is this structure gave rise to increased solubility. The *adj*-diphenanthroporphyrin system **30** was approached in a similar fashion (Scheme 8). Condensation of phenanthropyrroles **14a**, **14c**, or **14e** with dimethoxymethane in the presence of *p*-toluenesulfonic acid in acetic acid under a nitrogen atmosphere afforded the symmetrical dipyrrylmethanes **31** in excellent yields. These symmetrical dipyrrylmethanes were insufficiently soluble in $CDCl_3$ for NMR data to be obtained in this solvent, although **31c** had some solubility in d_6-DMSO and **31a** and **31b** dissolved to a limited extent in d_8-THF. The bridging methylene unit in these structures was considerably deshielded by the presence of two proximate phenanthrene ring systems and resonated near 5.5 ppm. The low solubility of the dibenzyl ester **31c** made this compound unsuitable for deprotection by hydrogenolysis,

(32) Chong, R.; Clezy, P. S.; Liepa, A. J.; Nichol, A. W. *Austr. J. Chem.* **1969**, *22*, 229.

Scheme 8



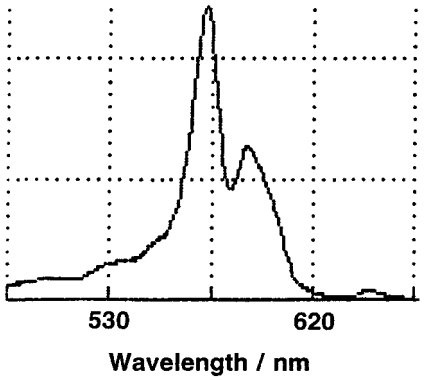
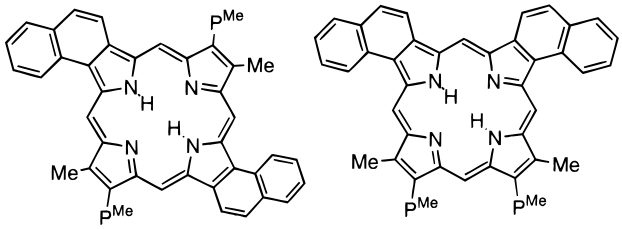


Figure 4. Electronic spectrum (Soret band excluded) of *opp*-diphenanthroporphyrin **27c** in chloroform.

and our attentions focused on the saponification of the diethyl or dimethyl ester counterparts. The ester units were conveniently cleaved with concomitant decarboxylation by refluxing **31a** or **31b** with KOH in ethylene glycol for 25 min with strict exclusion of oxygen. The deprotected dipyrrole **32** was immediately condensed with dialdehyde **22b** under standard conditions to give the targeted *adj*-diphenanthroporphyrin. Initially, poor yields of **30** were observed, but under more dilute conditions reasonable yields (18%) were obtainable. This porphyrin was insufficiently soluble in chloroform to obtain an NMR spectrum for the free base, although the data for the corresponding dication could be obtained in the presence of trifluoroacetic acid. The symmetry of this compound was confirmed by the proton NMR of the dication, and three separate resonances were observed for the *meso*-protons at 10.4 (1H), 11.4 (2H), and 12.3 (1H) ppm. Not surprisingly, the methine bridge proton flanked by two phenanthrene ring systems is further deshielded to below 12 ppm.

The UV-vis spectra for the free bases of *opp*-diphenanthroporphyrins **27b** and **27c** showed a Soret band at 428 nm and three Q-bands at 568, 591, and 645 nm, although the highest wavelength absorption was very weak (Figure 4). Poor solubility in the case of **27b** gave rise to slightly turbid green solutions in chloroform and this made molar

Chart 2. Dinaphthoporphyrins



33 **34**

P^{Me} = $CH_2CH_2CO_2Me$

absorptivity measurements difficult (sloping baselines were observed in this case), although dibutyl ester **27c** afforded clear green solutions and gave superior UV-vis data. The *adj*-diphenanthrene system **30** showed slightly longer wavelength shifts with a Soret band at 433 nm and four Q-bands at 536, 569, 594, and 652 nm. Both systems showed some significant similarities to the analogous *opp*- (**33**) and *adj*-dinaphthoporphyrins (**34**) (Chart 2),[18] and it is interesting to note that the adjacent ring fused structures gave the longer wavelength absorptions for both series. For **27b** and **27c**, Q-bands III and IV appear to have coalesced, bands II and III are separated by only 23 nm and band I has almost disappeared. While the shifts for the dinaphthoporphyrin counterpart **33** are less extreme (λ_{max} 425 (Soret), 530 (weak, Q_4), 564 (Q_3), 584 (Q_2) and 641 (Q_1) nm), and the Q_1 band is stronger, the same general features are present. The UV-vis spectra for *adj*-dinaphthoporphyrin **34** (λ_{max} 424 (Soret), 533 (Q_4), 566 (Q_3), 585 (Q_2), and 644 (Q_1) nm) and the related diphenanthroporphyrin **30** also show many similarities and exhibit a more typical four-banded pattern of Q absorptions. The dication of **27a** and **27b** showed a split Soret band at 436 and 458 nm, together with weaker absorptions at 581 and 638 nm, while the *adj*-diphenanthrene system **30** gave a single Soret absorption at 448 nm and longer wavelength bands at 584 and 632 nm. The nickel(II), copper(II), and zinc chelates of **30** were prepared, together with the zinc chelate of *opp*-diphenanthroporphyrin **27c** (only one metal complex was prepared in this case due to the limited quantities of material available). The nickel(II), copper(II), and zinc complexes of **30** showed the same trends previously noted for the monophenanthroporphyrin system **26**, although the molar extinction coefficients for the copper chelate could not be obtained due to its extremely poor solubility characteristics and the zinc complex only completely dissolved in the presence of trace pyrrolidine. The zinc chelate gave a relatively sharp Soret band at an anomolously high wavelength value of 453 nm (compared to 429 and 432 nm for Ni(II) and Cu(II) complexes, respectively), and the Q-bands were similarly shifted to unusually high values (Figure 5; λ_{max} 573 and 614 nm). The *opp*-diphenanthroporphyrin zinc chelate gave a similar result (Figure 5), although the bathochromic shifts were not as large in this case (λ_{max} 440 (Soret), 565, 614 nm). In this respect, the results parallel those for the free bases **27** and **30**, which also showed the larger red shifts in the adjacent ring fusion case. Clearly, distinct trends are emerging from these studies and further data may allow a deeper understanding of these results to be forthcoming.

These studies had demonstrated that porphyrins with two fused phenanthrene rings were easily synthesized and so we turned our attentions to the preparation of the tetraphenanthroporphyrin **10** (Scheme 9).[33] Reduction of ethyl ester **14a** with lithium aluminum hydride in THF at 0 °C afforded the unstable carbinol **35**,[34] and this was immediately cyclotetramerized to give the tetraphenanthrene-fused porphyrin **10**. Initially, we attempted to carry the chemistry out in refluxing pyridine-acetic acid,[35] but no detectable porphyrin products were formed under these conditions. However, by adapting the Lindsey conditions for tetraarylporphyrin synthesis, this moderately crowded porphyrin structure was attainable. Treatment of freshly prepared **35** with boron trifluoride etherate in chloroform generated the porphyrinogen **36**, and subsequent oxidation with DDQ afforded the symmetrical porphyrin system **10**. Following recrystallization from chloroform−methanol, this novel heptadecacycle was isolated as a greenish-black powder in 13% yield. It is notable that much poorer results were obtained when dichloromethane was used as a reaction solvent. This difference may be due to the presence of approximately 0.8% ethanol in the commercially available chloroform used for our studies as this can be a factor in tetraarylporphyrin formation.[36] Tetraphenanthroporphyrin **10** showed very little solubility in organic solvents, and UV-vis data could only be obtained for turbid partially dissolved and presumably aggregated material (λ_{max} (benzene) 430, 650, 704 nm). In the presence of 1% TFA, the system was diprotonated to give deep green solutions of the corresponding dication **10**H_2^{2+}. This species showed significant bathochromic shifts, with the Soret band appearing at 482 nm together with two weaker absorptions at 615 and 668 nm. These bands have been considerably shifted compared to the dications for mono- and diphenanthroporphyrins discussed above, although when one considers the degree of ring fusion these effects are surprisingly small. The proton NMR spectrum of **10**H_2^{2+} was consistent with a symmetrical structure, and the proton ring current was manifested in the observed chemical shifts. The *meso*-protons appeared downfield as a 4H singlet near 12.0 ppm, the deshielding being due in part to the proximity of two phenanthrene subunits. The high level of symmetry in **10**H_2^{2+} was particularly well illustrated in its carbon-13 NMR spectrum where the 68 carbon atoms in this structure gave rise to only nine resonances.

Conclusions

The "Barton−Zard" reaction of 9-nitrophenanthrene with esters of isocyanoacetic acid provides a convenient route to phenanthro[9,10-*c*]pyrroles **14** and these tetracyclic structures are easily converted into porphyrins with one, two, or four fused phenanthrene rings. The ring fusion induces limited bathochromic shifts in the electronic spectra of phenanthroporphyrins and their

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(34) (a) Ono, N.; Kawamura, H.; Bougauchi, M.; Maruyama, K. *Tetrahedron* **1990**, *46*, 7483. (b) Lash, T. D.; Balasubramaniam, R. P.; Catarello, J. J.; Johnson, M. C.; May, D. A., Jr.; Bladel, K. A.; Feeley, J. M.; Hoehner, M. C.; Marron, T. G.; Nguyen, T. H.; Perun, T. J., Jr.; Quizon, D. M.; Shiner, C. M.; Watson, A. *Energy Fuels* **1990**, *4*, 668. (c) May, D. A., Jr.; Lash, T. D. *J. Org. Chem.* **1992**, *57*, 4820. (d) Chen, S.; Lash, T. D. *J. Heterocycl. Chem.* **1997**, *34*, 273.

(35) Treibs, A.; Haberle, N. *Liebigs Ann. Chem.* **1968**, *450*, 164.

(36) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828. Lindsey, J. S.; MacCrum, K. A.; Tyhonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 9, 579.

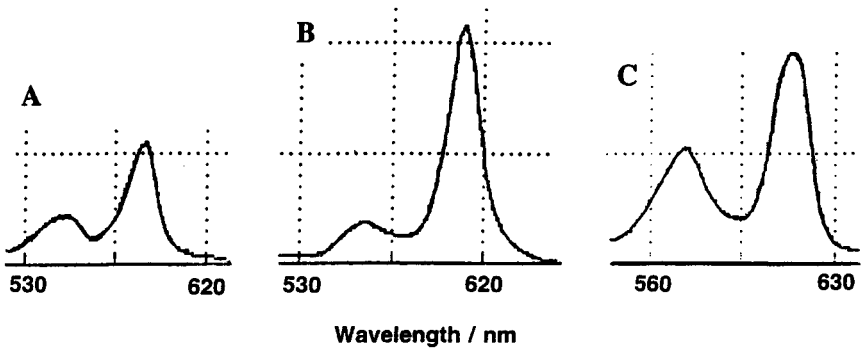
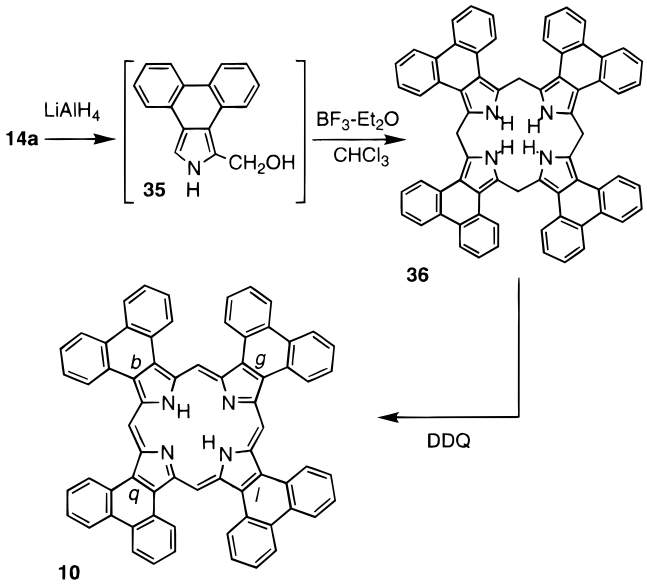


Figure 5. Electronic spectra (Soret bands excluded) of the zinc complexes of (A) monophenanthroporphyrin **19** in chloroform; (B) *opp*-diphenanthroporphyrin **27c** in chloroform; (C) *adj*-diphenanthroporphyrin **30** in trace pyrrolidine−chloroform.

Scheme 9



metal chelates, but these effects are smaller than might have been expected.[37] Nonetheless, some interesting trends are emerging from these studies and these could lead to applications (by analogy to the phthalocyanines) in the future.

Experimental Section[38]

tert-Butyl chloroacetate was obtained from Fluka Chemie AG; all other chemicals were purchased from Aldrich Chemical Co. and were not further purified unless otherwise indicated.

***tert*-Butyl *N*-Formylglycinate.** A mixture of formamide (200 mL) and sodium methoxide in methanol (prepared by reacting sodium (17.5 g) with 137 mL of methanol) was stirred in a 1 L round-bottomed flask at room temperature for 5 min. The flask was placed on a rotary evaporator for 2 h and then further evacuated overnight using a vacuum pump. The resulting oil was heated to 52 °C on a water bath. *tert*-Butyl chloroacetate (104.0 g) was added slowly, maintaining the reaction temperature at 55 °C throughout. After being stirred 4−6 h at room temperature, the mixture was poured into a cold sodium carbonate solution (60.0 g in 600 mL of water) and the heterogeneous mixture stirred at room-temperature overnight. If any solid formed, it was filtered off. The filtrate was extracted with dichloromethane (6 × 50 mL), and the combined organic extracts were washed with brine (2 × 30 mL) and then dried over sodium sulfate. The solvent was evaporated under reduced pressure and the product purified by distillation to give the N-formylglycinate (94.7 g; 92%) as a colorless liquid, bp 103−105 °C at 0.1−0.2 mmHg (lit.[39] bp 105 °C at 0.15mbar); IR (Nujol mull): ν 3335 (NH str), 1742, 1673 (C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.47 (9H, s), 3.97 (2H, d, J = 5.1 Hz), 6.18 (1H, br s), 8.23 (1H, s).

***tert*-Butyl Isocyanoacetate (13b).** A stirred solution of *tert*-butyl *N*-formylglycinate (60.60 g) and triethylamine (92.25 g) in dichloromethane (381 mL) were placed in a 3 L three-necked round-bottomed flask equipped with an addition funnel, thermometer, and drying tube, and the mixture was cooled to between −2 and 0 °C in an ice−salt bath. Freshly distilled phosphoryl chloride (58.29 g) was added dropwise, while the temperature was maintained at 0 °C. Once the addition was complete, the reddish-brown mixture was stirred at 0 °C for an additional 1 h. The ice−salt bath was replaced with an ice−water bath, and sodium carbonate solution (76.2 g in 305 mL water) was added at a sufficient rate to maintain the temperature of the mixture between 25 and 30 °C. The biphasic mixture was stirred for 30 min, after which water was added until the volume of the aqueous layer was brought up to 765 mL. The aqueous layer was separated and extracted with dichloromethane (2 × 200 mL). The combined organic extracts were washed with brine and dried over potassium carbonate. The solvent was evaporated under reduced pressure and the remaining brown oil distilled under reduce pressure to afford the isocyanoacetate (42.50 g; 80%) as a pale yellow liquid, bp 85.5−95 °C at 20 mmHg or 44−49 °C at 0.10 mmHg (lit. bp[40] 57 °C at 0.5 Torr); IR (Nujol mull): 162 (st, sh, C≡N), 1754 (st, sh, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.50 (9H, s), 4.13 (2H, s).

9-Nitrophenanthrene (12). Nitric acid (6 mL) was added dropwise (exothermic reaction) to a stirred acetic anhydride (12 mL). The resulting mixture was gradually added to a solution of phenanthrene (8.00 g) in glacial acetic acid (16 mL), moderating the rate of addition to avoid an overly vigorous reaction. The mixture was heated on a boiling water bath for 1−2 h and then poured into 500 mL of ice−water. The water was decanted off from the resulting yellow gum, and the residue was dissolved in chloroform (75 mL). The ice−water solution was extracted with 50 mL of chloroform, and the combined organic solutions were washed sequentially with water (25 mL), 5% aqueous sodium bicarbonate solution (25 mL), and water (25 mL). The organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was taken up in a small amount of toluene and loaded on a column (41 mm internal diameter × 250 mm) of grade 3 alumina and eluted with hexanes. After the yellow nitrophenanthrene fraction started to elute, approximately 2.0 L of hexanes was collected. Evaporation of the solvent under reduced pressure, followed by recrystalli-

(37) (a) Lin, Y.; Lash, T. D. *Tetrahedron Lett.* **1995**, *36*, 9441. (b) Chandrasekar, P.; Lash, T. D. *Tetrahedron Lett.* **1996**, *37*, 4873. (c) Lash, T. D.; Chandrasekar, P. *J. Am. Chem. Soc.* **1996**, *118*, 8767.

(38) For general experimental procedures, see ref 1.

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(40) Ugi, I.; Betz, W.; Fetzer, U.; Offermann, K. *Chem. Ber.* **1961**, *94*, 2814.

zation from 95% ethanol, gave the desired nitrophenanthrene isomer (2.24 g; 22%) as yellow crystals, mp 117 °C (lit. mp[28] 116−117 °C). ^{1}H NMR ($CDCl_3$): δ 7.68−7.86 (4H, m), 8.02 (1H, d, J = 7.9 Hz), 8.48 (1H, s), 8.49−8.52 (1H, m), 8.71 (1H, d, J = 7.9 Hz), 8.76−8.79 (1H, m).

Ethyl Phenanthro[9,10-*c*]pyrrole-1-carboxylate (14a). DBU (1.596 g) was added dropwise to a solution of ethyl isocyanoacetate[41] (1.185 g) and 9-nitrophenanthrene (2.339 g) in THF (20 mL), and the resulting mixture was stirred at room-temperature overnight. The solution was diluted with chloroform, washed with water, and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue recrystallized from toluene to give the pyrrole (2.376 g; 78%) as yellow crystals, mp 177−178 °C; IR (Nujol mull): ν 3297 (NH str), 1659 (C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.47 (3H, t, J = 7.2 Hz), 4.48 (2H, q, J = 7.2 Hz), 7.58 (2H, m), 7.67 (2H, m), 7.86 (1H, d, J = 3 Hz), 8.15 (1H, m), 8.60 (2H, m), 9.85 (1H, m), 10.0 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 14.6, 60.7, 114.9, 116.1, 122.8, 122.9, 123.1, 123.5, 124.0, 125.8, 126.8, 127.0, 127.1, 127.5, 128.4, 128.9, 130.5, 160.6; EI MS: *m*/*z* (% rel abund) 289 (52; [M$^+$]), 243 (100; [M − EtOH]$^+$). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.22; N, 4.84. Found: C, 79.18; H, 5.34; N, 4.85.

***tert*-Butyl Phenanthro[9,10-*c*]pyrrole-1-carboxylate (14d).** Over a period of 5 min, DBU (1.796 g) was added dropwise to a stirred mixture of 9-nitrophenanthrene (1.32 g) and *tert*-butyl isocyanoacetate (0.832 g) in THF (15 mL) and 2-propanol (15 mL). The solution was stirred overnight at room temperature, diluted with chloroform, washed with 25 mL of water, and dried over sodium sulfate. The solvent was evaporated and the residual oil taken up in a small amount of hexanes and loaded onto a silica gel eluting with hexanes. After unreacted 9-nitrophenanthrene had eluted from the column, the solvent was switched to toluene, and a major product fraction was collected. Recrystallization from carbon tetrachloride gave the phenanthropyrrole (1.143 g; 61%) as pale yellow crystals, mp 178 °C. An analytical sample was obtained by recrystallization from toluene as yellow crystals, mp 176 °C (softens at 170 °C). IR (Nujol mull): ν 3297 (NH str), 1659 (C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.70 (9H, s), 7.46−7.63 (4H, m), 7.74 (1H, d, J = 3.3 Hz), 8.05−8.08 (1H, m), 8.50−8.57 (2H, m), 9.76 (1H, d, J = 7.8 Hz), 9.86 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 28.6, 81.8, 114.1, 117.6, 122.9, 123.1, 123.3, 123.5, 125.7, 126.6, 126.9, 127.0, 127.7, 128.6, 128.9, 130.9, 160.3; EI MS: *m*/*z* (% rel abund) 317 (21; [M$^+$]), 261 (50; [M − $(CH_3)_2C{=}CH_2$]$^+$), 243 (100; [M − *t*-BuOH]$^+$). Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.33; H, 5.92; N, 4.13.

Benzyl Phenanthro[9,10-*c*]pyrrole-1-carboxylate (14e). Benzyl isocyanoacetate[24] (2.395 g) and 9-nitrophenanthrene (2.730 g) were dissolved in anhydrous THF (30 mL). DBU (2.235 g) was added dropwise over several minutes, and the resulting mixture was heated under reflux overnight. The organic phase was diluted with chloroform, washed with water, and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue taken up in a small amount of toluene and loaded on a silica gel column. The column was eluted with toluene, and a yellow band was collected. Recrystallization from carbon tetrachloride gave the phenanthropyrrole (3.737 g; 87%), as pale yellow crystals, mp 185−186 °C; IR (Nujol mull): ν 3425 (NH str), 1696 (C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.44 (2H, s), 7.37−7.59 (9H, m), 7.77 (1H, d, J = 3.3 Hz), 8.05−8.08 (1H, m), 8.50−8.57 (2H, m), 9.77−9.79 (1H, m), 9.80 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 66.6, 115.3, 115.6, 122.9, 123.2, 123.5, 125.8, 126.9, 127.1, 127.1, 127.4, 127.5, 128.5 (2), 128.8, 128.9, 130.6, 136.0, 160.0; EI MS: *m*/*z* (% rel abund) 351 (68; [M$^+$]), 243 (47; [M − BnOH]$^+$), 91 (100). Anal. Calcd for $C_{24}H_{17}NO_2{\cdot}{}^1/_5H_2O$: C, 81.20; H, 4.94; N, 3.94. Found: C, 81.20; H, 4.87; N, 3.87.

Methyl Phenanthro[9,10-*c*]pyrrole-1-carboxylate (14c). The foregoing reaction of **13c** (1.962 g) and **12** (2.237 g) was carried out in refluxing methanol (15 mL)−THF (15 mL). Recrystallization from carbon tetrachloride gave the methyl ester **14c** (1.489 g; 54%) as a white powder, mp 193−194 °C; IR (Nujol mull): ν 3431 (NH str), 1698 (C=O str), 760 (phenanthrene-H out-of-plane bending) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.00 (3H, s), 7.50−7.66 (4H, m), 7.76 (1H, d, J = 3.3 Hz), 8.05−8.08 (1H, m), 8.51−8.59 (2H, m), 9.77−9.81 (1H, m), 9.90 (1H, br s); ^{1}H NMR (d_8-THF): δ 3.94 (3H, s), 7.44−7.54 (4H, m), 7.96 (1H, d, J = 3.3 Hz), 8.17−8.20 (1H, m), 8.54−8.62 (2H, m), 9.89−9.93 (1H, m), 11.97 (1H, br s); ^{1}H NMR (d_6-DMSO−$CDCl_3$): δ 3.95 (3H, s), 7.4−7.54 (4H, m), 7.84 (1H, d, J = 3.6 Hz), 8.06−8.09 (1H, m), 8.45−8.52 (2H, m), 9.72−9.76 (1H, m), 12.17 (1H, br s); ^{13}C NMR (d_6-DMSO−$CDCl_3$): δ 50.5, 114.6, 115.6, 121.2, 122.2, 122.3, 122.5, 122.9, 124.8, 125.8, 126.0, 126.5, 127.0 (2), 127.4, 127.5, 129.4, 160.7; EI MS: *m*/*z* (% rel abund) 275 (59; [M$^+$]), 243 (100; [M − MeOH]$^+$). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.36; H, 4.84; N, 5.09.

Ethyl 3-Bromophenanthro[9,10-*c*]pyrrole-1-carboxylate (16). Bromine (0.14 g) was added dropwise to a stirred solution of **14a** (0.25 g) in acetic acid, and the resulting solution stirred at room temperature for 10 min. The solution was diluted with chloroform and washed with water, 5% sodium bicarbonate solution and water. The solution was dried over sodium sulfate, filtered, and evaporated under reduced pressure. The residue was recrystallized from chloroform−hexanes to give the 3-bromo derivative (0.26 g; 81%) as pale yellow microneedles, mp 163 °C, dec (sample starts to darken at 120 °C); IR (Nujol mull): ν 3220 (NH str), 1656 (C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.49 (3H, t, J = 7.2 Hz), 4.49 (2H, q, J = 7.2 Hz), 7.51−7.62 (4H, m), 8.52−8.56 (2H, m), 8.98−9.02 (1H, m), 9.73−9.77 (1H, m), 9.81 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 14.7, 61.3, 98.6, 116.8, 119.2, 122.7, 123.4, 123.7, 126.0, 126.6, 127.0, 127.0, 127.2, 127.4, 127.7, 128.6, 129.9, 130.9, 160.1. Anal. Calcd for $C_{19}H_{14}BrNO_2$: C, 61.97; H, 3.83; N, 3.80. Found: C, 61.24; H, 3.91; N, 3.66.

Benzyl 3-((5-(Benzyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (17b). Method A: *p*-Toluenesulfonic acid (13 mg) was added to a stirred mixture of benzyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14e**; 250 mg) and benzyl 5-(acetoxymethyl)-4-ethyl-3-methylpyrrole-2-carboxylate[42] (**18a**; 224 mg) in glacial acetic acid (25 mL). The mixture was stirred at room temperature for 2 h, and the solution was then poured into 250 mL ice/water and allowed to stand for a further 2 h. The mixture was extracted with chloroform, and the organic layer was washed with 3 × 25 mL of portions water, 5% sodium bicarbonate solution (25 mL), and water (25 mL) and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the solid residue recrystallized from carbon tetrachloride to give the dipyrrylmethane (347 mg; 80%) as white crystals, mp 182−183 °C; IR (Nujol mull): ν 3412, 3301 (2 × NH str), 1710, 1668 (2 × C=O str) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.01 (3H, t, J = 7.5 Hz), 2.31 (3H, s), 2.41 (2H, q, J = 7.5 Hz), 4.53 (2H, s), 5.22 (2H, s), 5.33 (2H, s), 7.29−7.33 (10H, m), 7.49−7.58 (4H, m), 8.03−8.04 (1H, m), 8.53−8.56 (2H, m), 8.67 (1H, br s), 9.38 (1H, br s), 9.79−9.77 (1H, m); ^{13}C NMR ($CDCl_3$): δ 10.6, 15.2, 17.3, 27.1, 65.7, 66.3, 113.0, 118.0, 118.5, 123.0, 123.4, 123.7, 125.2, 125.5, 126.3, 126.5, 126.7, 127.1, 127.4, 127.7, 128.0 (2), 128.2, 128.3, 128.5, 128.6, 129.5, 130.4, 135.9, 159.9, 161.2; EI MS: *m*/*z* (% rel abund) 606 (23; [M$^+$]), 504 (63), 91 (100). Anal. Calcd for $C_{40}H_{34}N_2O_4{\cdot}{}^1/_2H_2O$: C, 78.03; H, 5.73; N, 4.55. Found: C, 77.68; H, 5.51; N, 4.46.

Method B: A solution of **14e** (100 mg) and **18a** (90 mg) in dichloromethane (10 mL) was stirred vigorously with Montmorillonite clay (520 mg) for 16 h. The catalyst was filtered off and washed with dichloromethane, and the combined organic solutions were evaporated under reduced pressure. Recrystallization from carbon tetrachloride gave the dipyrrylmethane (160 mg; 93%) as pink crystals, mp 180−182 °C.

***tert*-Butyl 3-((5-(*tert*-Butoxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-car-

(41) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1979**, *59*, 183.

(42) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1959**, 3416.

boxylate (17a). The dipyrrylmethane was prepared from *tert*-butyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14d**; 1.00 g) and *tert*-butyl 5-(acetoxymethyl)-4-ethyl-3-methylpyrrole-2-carboxylate[43] (**18b**; 0.887 g) by method A. The reaction mixture was poured into ice/water (350 mL) and the resulting precipitate collected by suction filtration. Recrystallization from methanol gave the dipyrrylmethane (1.445 g; 85%) as pink crystals, mp 191−192 °C; IR (Nujol mull): ν 3424 (NH str), 1696 (C═O str) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.09 (3H, t, J = 7.5 Hz), 1.51 (9H, s), 1.59 (9H, s), 2.33 (3H, s), 2.48 (2H, q, J = 7.5 Hz), 4.55 (2H, s), 7.48−7.62 (4H, m), 8.08−8.11 (1H, m), 8.54−8.61 (3H, m), 9.29 (1H, br s), 9.73−9.77 (1H, m); ^{13}C NMR ($CDCl_3$): δ 10.5, 15.3, 17.4, 27.1, 28.5, 28.7, 80.7, 81.3, 114.6, 117.8, 120.1, 122.9, 123.4, 123.7, 125.1, 125.2, 125.6, 125.7, 126.3, 126.7, 126.9, 127.0, 127.7, 128.5, 128.6, 129.5, 130.3, 159.8, 161.1. Anal. Calcd for $C_{34}H_{38}N_2O_4 \cdot {}^1/_2H_2O$: C, 74.56, H, 6.99; N, 5.11. Found: C, 74.54; H, 7.04; N, 5.05.

Ethyl 3-((5-(Ethoxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (17c). Prepared by method A from **14a** (0.500 g) and ethyl 5-(acetoxymethyl)-4-ethyl-3-methylpyrrole-2-carboxylate (**18c**; 0.438 g). Recrystallization from ethanol gave the diethyl ester **17c** (0.725 g; 87%) as fluffy pale pink crystals, mp 219 °C (softens at 210 °C); IR (Nujol mull): ν 3425, 3300 (2 × NH str), 1713, 1653 (2 × C═O str) cm^{-1}; ^1H NMR (d_6-DMSO−$CDCl_3$): δ 0.89 (3H, t, J = 7.5 Hz), 1.28 (3H, t), 1.43 (3H, t, J = 7 Hz), 2.21 (3H, s), 2.41 (2H, q, J = 7.5 Hz), 4.20 (2H, q, J = 7 Hz), 4.42 (2H, q, J = 7 Hz), 4.62 (2H, s), 7.44−7.58 (4H, m), 8.15−8.18 (1H, m), 8.50−8.54 (2H, m), 9.73−9.76 (1H, m), 10.49 (1H, br s), 11.55 (1H, br s); ^{13}C NMR (d_6-DMSO−$CDCl_3$): δ 9.1, 13.3, 14.0, 15.8, 24.7, 58.0, 59.0, 112.2, 116.5, 116.7, 121.9, 122.3, 122.6, 122.8, 123.7, 125.1, 125.6, 126.5, 127.1, 127.4, 127.5, 127.7, 129.0, 159.7, 160.4. Anal. Calcd for $C_{30}H_{30}N_2O_4$: C, 74.67; H, 6.26; N, 5.80. Found: C, 74.57; H, 6.03; N, 5.75.

Benzyl 3-((5-(*tert*-Butoxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (17d). The title dipyrrylmethane was prepared by method A from **14e** (300 mg) and *tert*-butyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate[43] (**18b**; 240 mg). Recrystallization from carbon tetrachloride gave the dipyrrylmethane (363 mg; 74%) as pink crystals, mp 193−194 °C, dec (mp ≈130 °C with rapid heating). Method B similarly gave the dipyrrylmethane in 85% yield. IR (Nujol mull): ν 3444, 3241 (NH str), 1710, 1654 (C═O str) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.04 (3H, t, J = 7.5 Hz), 1.53 (9H, s), 2.32 (3H, s), 2.44 (2H, q, J = 7.5 Hz), 4.57 (2H, s), 5.37 (2H, s), 7.36−7.44 (5H, m), 7.52−7.61 (4H, m), 8.09−8.11 (1H, m), 8.57−8.62 (3H, m), 9.45 (1H, br s), 9.79−9.83 (1H, m); ^{13}C NMR ($CDCl_3$): δ 10.6, 15.2, 17.3, 27.1, 28.5, 51.6, 80.7, 113.1, 115.0, 118.0, 120.1, 122.8, 123.0, 123.1, 123.4, 123.5, 123.7, 125.1, 125.2, 125.4, 125.8, 126.0, 126.3, 126.6, 126.8, 127.0 (2), 127.2, 127.4, 128.3, 129.5, 130.5, 160.7, 161.2. Anal. Calcd for $C_{37}H_{36}N_2O_4 \cdot {}^1/_2H_2O$: C, 76.39; H, 6.41; N, 4.81. Found: C, 76.04; H, 6.26; N, 4.74.

***tert*-Butyl 3-((5-(Benzyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (17e).** The dipyrrylmethane was prepared by method A from *tert*-butyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14d**; 1.00 g) and **18a**[42] (0.994 g). Recrystallization from carbon tetrachloride gave the required dipyrrylmethane (1.23 g; 68%) as pale orange crystals, mp 192−193 °C; IR (Nujol mull): ν 3424 (NH str), 1696 (C═O str) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.08 (3H, t, J = 7.5 Hz), 1.56 (9H, s), 2.35 (3H, s), 2.46 (2H, q, J = 7.5 Hz), 4.53 (2H, s), 5.20 (2H, s), 7.28 (5H, s), 7.48−7.61 (4H, m), 8.02−8.05 (1H, m), 8.52−8.57 (2H, m), 8.84 (1H, br s), 9.29 (1H, br s), 9.75 (1H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$): δ 10.6, 15.3, 17.3, 27.1, 28.4, 65.7, 81.4, 114.7, 117.8, 118.4, 122.9, 123.3, 123.7, 125.1, 125.2, 125.4, 126.7, 126.9, 127.0, 127.7 (2), 128.0 (2), 128.4, 128.5, 129.4, 130.3, 136.2, 159.8, 161.3. Anal. Calcd for $C_{37}H_{36}N_2O_4 \cdot {}^1/_4H_2O$: C, 76.99; H, 6.37; N, 4.85. Found: C, 76.92; H, 6.39; N, 4.85.

(43) Clezy, P. S.; Crowley, R. J.; Hai, T. T. *Aust. J. Chem.* **1982**, *35*, 411.

Benzyl 3-((5-(*tert*-Butoxycarbonyl)-3-(2-(methoxycarbonyl)ethyl)-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (17f). The dipyrrylmethane was prepared by method A from **14e** (200 mg) and *tert*-butyl 5-(acetoxymethyl)-4-(2-(methoxycarbonyl)ethyl)-3-methylpyrrole-2-carboxylate[44] (**18d**; 193 mg). Recrystallization from 95% ethanol gave the desired dipyrrylmethane (191 mg; 53%) as pale pink crystals. Method B afforded the mixed ester species **17f** in 80% yield, mp 165−167 °C. IR (Nujol mull): ν 3423, 3305 (2 × NH str), 1753, 1701, 1660 (3 × C═O str) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.41 (9H, s), 2.27 (3H, s), 2.51 (2H, t, J = 6.9 Hz), 2.77 (2H, t, J = 6.9 Hz), 3.51 (3H, s), 4.68 (2H, s), 5.41 (2H, s), 7.35−7.42 (5H, m), 7.51−7.55 (2H, m), 7.59−7.61 (2H, m), 8.18−8.21 (1H, m), 8.50 (1H, br s), 8.56−8.65 (2H, m), 9.79−9.83 (1H, m), 10.05 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.5, 19.1, 26.5, 28.3, 51.6, 66.3, 80.6, 113.2, 118.3, 120.1, 120.6, 122.8, 123.0, 123.8, 123.9, 125.4, 126.1, 126.2, 127.0 (2), 127.2, 127.4, 127.5, 128.0, 128.1, 128.2, 128.4, 128.6, 129.6, 130.5, 136.1, 160.1, 160.2, 173.8. Anal. Calcd for $C_{38}H_{38}N_2O_6$: C, 74.27; H, 6.07; N, 4.44. Found: C, 74.40; H, 6.12; N, 4.19.

Benzyl 3-((3-Ethyl-5-formyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (28a). Benzyl 3-((5-(*tert*-butyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl-)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (190 mg) was dissolved in TFA (8 mL) and placed on a warm water bath (45−50 °C) for 20 min. The solution was diluted with 15 mL of dichloromethane, washed with water (25 mL), 5% $NaHCO_3$ solution (25 mL), and water (25 mL), and dried over sodium sulfate. The solvent was evaporated, and the resulting oil was taken up in 2.0 mL of DMF and placed in a 10 mL round-bottom flask. The mixture was cooled in an ice/salt bath to 0 °C. Benzoyl chloride (0.19 mL) was added dropwise, maintaining the temperature of the mixture at 0 °C. After the addition was completed, the temperature was allowed to drop to −5 °C, and then the ice/salt bath was removed and stirring continued at room temperature for 1 h. The flask was then cooled with an ice/salt bath, 2.0 mL of toluene was added, and the mixture allowed to stir for an additional 1 h. The intermediary imine salt oiled out, so the solvents were removed on a rotary evaporator, initially using a water aspirator and then at oil pump pressures. The residual oil was taken up in a 50:50 mixture of ethanol/water (5 mL), sodium carbonate (190 mg) was added, and the mixture was stirred on a boiling water bath for 15 min. Water (7 mL) was added, and the mixture was allowed to stand at room-temperature overnight. The resulting precipitate was filtered off and recrystallized from chloroform/petroleum ether to give the monoaldehyde (100 mg; 60%) as light brown crystals, mp 188 °C, dec; ^1H NMR ($CDCl_3$): δ 1.07 (3H, t, J = 7.6 Hz), 2.29 (3H, s), 2.47 (2H, q, J = 7.6 Hz), 4.58 (2H, s), 5.34 (2H, s), 7.32−7.38 (5H, m), 7.49−7.62 (4H, m), 7.97−8.01 (1H, m), 8.54−8.61 (2H, m), 8.86 (1H, br s), 9.50 (1H, s), 9.59 (1H, br s), 9.76−9.79 (1H, m); ^{13}C NMR ($CDCl_3$): δ 10.5, 18.4, 19.1, 26.2, 28.3, 34.3, 51.5, 51.6, 58.4, 80.5, 113.4, 118.2, 120.0, 120.3, 122.6, 123.0, 123.9, 125.3, 125.9, 126.0, 126.9 (2), 127.0, 127.2, 127.5, 127.7, 128.3, 129.6, 130.4, 160.7, 160.9, 174.0. HR MS (EI): Calcd for $C_{33}H_{28}N_4O_3$: m/z 500.20999. Found: 500.21057.

3-((5-(Benzyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl-)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxaldehyde. *tert*-Butyl 3-((5-(benzyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl-)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (**17e**; 200 mg) was taken up in TFA (0.96 mL) and stirred at room temperature for 15 min. The solution was cooled to 0 °C with a salt−ice bath, and trimethyl orthoformate (0.3 mL) was added dropwise, maintaining the temperature at 0 °C throughout. The mixture was stirred at room temperature for 5 min and poured into 10 mL of water. The resulting precipitate was suction filtered and recrystallized from chloroform to give the aldehyde (45 mg; 26%) as white crystals, mp 268 °C, dec; ^1H NMR ($CDCl_3$): δ 1.10 (3H, t, J = 7.4 Hz), 2.36 (3H, s), 2.45 (2H, q, J = 7.4 Hz), 4.62 (2H, s), 5.21 (2H, s), 7.32 (5H, m), 7.56−7.66 (4H, m), 8.11−8.15 (1H, m), 8.45−8.49 (1H, m), 8.62

(44) Clezy, P. S.; Liepa, A. J. *Aust. J. Chem.* **1970**, *23*, 2443.

(2H, d, J = 8 Hz), 8.77 (1H, br s), 9.68 (1H, br s), 10.37 (1H, s); EI MS: m/z (% rel abund) 500 (100; [M^+]). HR MS (EI): Calcd for $C_{33}H_{28}N_4O_3$: m/z 500.20999. Found: 500.20985. Anal. Calcd for $C_{33}H_{28}N_2O_3$: C, 79.18; H, 5.64; N, 5.60. Found: C, 79.08; H, 5.55; N, 5.59.

Benzyl 3-((5-Formyl-3-(2-(methoxycarbonyl)ethyl)-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (28b). The monoaldehyde was prepared by the method described for **28a** from benzyl 3-((5-(*tert*-butyloxycarbonyl)-3-ethyl-4-(2-(methoxycarbonyl)ethyl)-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (**17f**; 191 mg). Recrystallization from chloroform/petroleum ether gave the monoaldehyde (96 mg; 57%) as pale brown crystals, mp 223−224 °C; ^{1}H NMR ($CDCl_3$): δ 2.26 (3H, s), 2.51 (2H, t, J = 6.8 Hz), 2.76 (2H, t, J = 6.8 Hz), 3.53 (3H, s), 4.68 (2H, s), 5.37 (2H, s), 7.32−7.59 (9H, m), 8.03−8.06 (1H, m), 8.54−8.60 (2H, m), 8.92 (1H, br s), 9.43 (1H, s), 9.75−9.78 (1H, m), 10.17 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 8.9, 18.9, 26.8, 34,1, 51.8, 66.5, 113.8, 118.8, 121.4, 122.8, 123.1, 123.9, 125.5, 125.8, 126.2, 127.1, 127.3, 127.4, 128.1, 128.4, 128.5, 128.7, 129.0, 129.9, 130.5, 131.4, 133.1, 136.1, 160.2, 173.9, 176.5. Anal. Calcd for $C_{35}H_{30}N_2O_5 \cdot H_2O$: C, 72.90; H, 5.59; N, 4.86. Found: C, 73.10; H, 5.58; N, 4.80.

Dibenzyl 1,1′-Diphenanthro[9,10-*c*]pyrrolylmethane-3,3′-dicarboxylate (31c). Benzyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14e**; 300 mg), dimethoxymethane (65 mg), and *p*-toluenesulfonic acid (30 mg) were dissolved in 30 mL of glacial acetic acid. The reaction vessel was purged with nitrogen, and the mixture was stirred under an atmosphere of nitrogen at room temperature for 3 days. The cloudy mixture was poured into 300 mL of ice/water and allowed to stand for 2 h. The resulting precipitate was extracted with THF, washed with 25 mL of water, 25 mL of 5% sodium bicarbonate solution, and 25 mL of water, and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue recrystallized from THF/hexanes to give the dipyrrylmethane (252 mg; 83%) as pale purple crystals, mp > 300 °C; IR (Nujol mull): ν 3439 (NH str), 1711 (C═O str) cm^{-1}; ^{1}H NMR (d_6-DMSO): δ 5.31 (4H, s), 5.53 (2H, s), 7.18−7.26 (10H, m), 7.37−7.63 (8H, m), 8.17 (2H, m), 8.66−8.71 (4H, m), 9.73 (2H, d, J = 9.2 Hz), 11.81 (2H, br s); ^{13}C NMR (d_6-DMSO): δ 28.8, 51.5, 113.3, 117.7, 123.3, 123.6, 124.4, 125.2, 126.8, 126.9, 127.1, 127.4, 127.7, 128.5, 129.8, 160.9; HR MS (EI): Calcd for $C_{49}H_{34}N_2O_4$: m/z 714.2510. Found: 714.2524.

Diethyl 1,1′-Diphenanthro[9,10-*c*]pyrrolylmethane-3,3′-dicarboxylate (31a). The dipyrrylmethane was prepared by the procedure given for **31c** from ethyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14a**; 500 mg), dimethoxymethane (132 mg), and *p*-toluenesulfonic acid (50 mg). Recrystallization from toluene gave the dipyrrylmethane (343 mg; 67%) as off-white crystals, mp > 300 °C; IR (Nujol mull): ν 3395 (NH str), 1704, 1638 (C═O str) cm^{-1}; ^{1}H NMR (d_8-THF): δ 1.08 (6H, t, J = 7 Hz), 4.19 (4H, q, J = 7 Hz), 5.47 (2H, s), 7.45−7.59 (8H, m), 8.24−8.26 (2H, m), 8.64−8.70 (4H, m), 9.90−9.94 (2H, m), 10.86 (2H, br s); HR MS (EI): Calcd for $C_{39}H_{30}N_2O_4$: m/z 590.2198. Found: 590.2200. Anal. Calcd for $C_{39}H_{30}N_2O_4 \cdot {}^1/_2H_2O$: C, 78.11; H, 5.21; N, 4.67. Found: C, 77.87; H, 4.89; N, 4.45.

Dimethyl 1,1′-Diphenanthro[9,10-*c*]pyrrolylmethane-3,3′-dicarboxylate (31b). The dipyrrylmethane was prepared from methyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (**14c**; 500 mg) by the procedure given for **31c**. Recrystallization from toluene gave the dipyrrylmethane (423 mg; 83%) as off-white crystals, mp 283 °C, dec; IR (Nujol mull): ν 3409 (NH str), 1713, 1645 (C═O str) cm^{-1}; ^{1}H NMR (d_8-THF): δ 3.75 (6H, s), 5.45 (2H, s), 7.40−7.58 (8H, m), 8.20−8.23 (2H, m), 8.64−8.70 (4H, m), 9.92−9.96 (2H, m), 10.93 (2H, br s); ^{13}C NMR (d_8-THF): δ 30.6, 51.7, 115.4, 119.6, 124.1, 124.6, 124.8, 126.2, 126.6, 126.8, 127.8, 128.3, 129.0, 129.6, 129.7, 130.8, 131.8, 161.7. Anal. Calcd for $C_{37}H_{26}N_2O_4 \cdot {}^3/_5H_2O$: C, 77.50; H, 4.78; N, 4.88. Found: C, 77.28; H, 4.35; N, 4.84.

7,13,17-Triethyl-8,12,18-trimethylphenanthro[9,10-*b*]porphyrin (19). (a) *tert*-Butyl 3-((5-(*tert*-butoxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (**17a**; 200 mg) was dissolved in 4 mL of TFA and stirred at room temperature for 15 min. The resulting solution was diluted with dichloromethane (25 mL), washed with water (15 mL), 5% sodium bicarbonate solution (15 mL), and water (15 mL), and dried over sodium sulfate. The solvent was evaporated under reduced pressure, and the crude residue was dissolved in dichloromethane (44 mL) and methanol (1.5 mL). 3,3′-Diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane-5,5′-dicarboxaldehyde[1] (**22a**; 101 mg) was added to the mixture, followed by 400 mg of *p*-toluenesulfonic acid dissolved in 1.5 mL of methanol, and the solution was allowed to stir in the dark at room-temperature overnight. The following day, a saturated solution of zinc acetate (12 mL) in methanol was added and the mixture stirred in the dark at room-temperature overnight. The solvent was evaporated under reduced pressure. The residue was taken up in a small amount of dichloromethane, loaded onto a column of grade 3 alumina, and eluted with dichloromethane. A red fraction was collected, the solvent evaporated, and the residue taken up in a small amount of TFA. The mixture was diluted with dichloromethane and washed with water (15 mL), 5% aqueous sodium bicarbonate solution (15 mL), and water (15 mL). The solvent was evaported under reduced pressure, and the residue was chromatographed on grade 3 alumina, eluting with toluene. The product fraction was collected as a dark maroon band. Recrystallization from chloroform/methanol gave the monophenanthroporphyrin (24 mg; 12%) as dark purple crystals, mp >300 °C.

(b) Benzyl 3-((5-(benzyloxycarbonyl)-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (200 mg) was dissolved in THF (15 mL) in a hydrogenation vessel and diluted with anhydrous methanol (100 mL). Triethylamine (10 drops) was added to the mixture, and the vessel was flushed with nitrogen. Palladium/charcoal (10%; 50 mg) was cautiously added, and the reaction mixture was shaken under an atmosphere of hydrogen at 45 psi overnight. The catalyst was filtered off and the solvent evaporated under reduced pressure. Residual traces of triethylamine were removed under high vacuum. The residue was reacted with **22a**[1] (90 mg) and *p*-toluenesulfonic acid (0.394 g) under the conditions described above. Recrystallization from chloroform/methanol gave the required porphyrin (54 mg; 29%) as dark purple crystals, mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 417 (5.23), 516 (4.02), 553 (4.47), 577 (4.11), 634 nm (3.58); UV-vis (1% TFA−CH_2Cl_2): λ_{max} (log ϵ) 403 (5.13), 420 (5.17), 566 (4.26), 612 nm (4.26); ^{1}H NMR ($CDCl_3$): δ −4.00 (2H, br s), 1.82−1.88 (9H, m), 3.50 (3H, s), 3.59 (3H, s), 3.60 (3H, s), 3.93−4.08 (6H, m), 7.83−7.89 (2H, m), 8.00−8.07 (2H, m), 9.05 (2H, d, J = 8.3 Hz), 9.79−9.88 (4H, m), 10.74 (2H, s); HR MS (FAB): Calcd for $C_{41}H_{38}N_4$ + H: m/z 587.3166; found 587.3178. Nickel(II) complex: maroon crystals (chloroform−methanol), mp > 300 °C; UV-vis ($CHCl_3$): λ_{max} (log ϵ) 412 (5.13), 534 (3.90), 578 nm (4.47). Copper(II) complex: reddish brown crystals (chloroform−methanol), mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 414 (5.41), 540 (4.02), 585 nm (4.51). Zinc complex: purple crystals (chloroform−methanol), mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 418 (5.42), 550 (4.14), 590 nm (4.52).

13,17-Dibutyl-7-ethyl-8,12,18-trimethylphenanthro[9,10-*b*]porphyrin (20). Dibenzyl ester **17b** (100 mg) was hydrogenolyzed as described above in procedure b. The resulting crude dicarboxylic acid was dissolved with 3,3′-dibutyl-4,4′-dimethyl-2,2′-dipyrrylmethane-5,5′-dicarboxaldehyde[1] (**22b**; 52 mg) in dichloromethane (180 mL) and methanol (8 mL), *p*-toluenesulfonic acid (0.35 g) in methanol (8 mL) was added, and the resulting mixture was stirred in the dark at room temperature for 16 h. A saturated solution of zinc acetate in methanol (8 mL) was added and the solution stirred at room temperature for a further 24 h. Following the standard workup (as above), recrystallization from chloroform/methanol gave the required phenanthroporphyrin (36 mg; 37%) as dark purple crystals, mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 416 (5.24), 512 (4.01), 555 (4.48), 576 (4.12), 633 (3.61) nm; ^{1}H NMR ($CDCl_3$): δ −3.85 (2H, br s), 1.10−1.17 (6H, m), 1.71−1.82 (4H, m), 1.89 (3H, t, J = 7.6 Hz), 2.19−2.31 (4H, m), 3.51 (3H, s), 3.60 (3H, s), 3.62 (3H, s), 3.92 (2H, t, J = 7.6 Hz), 4.03

(2H, t, J = 7.5 Hz), 4.10 (2H, q, J = 7.6 Hz), 7.89 (2H, t), 8.05−8.09 (2H, m), 9.08 (2H, d, J = 8.3 Hz), 9.87−9.91 (4H, m), 10.83 (1H, s), 10.85 (1H, s); HR MS (FAB): Calcd for $C_{45}H_{46}N_4$ + H: *m*/*z* 643.3790. Found: 643.3800.

7,17-Diethyl-8,18-dimethyldiphenanthro[9,10-*b*:9,10-*l*]porphyrin (27a). Benzyl 3-((5-formyl-3-ethyl-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (**27a**; 100 mg) was placed in a hydrogenation vessel and dissolved in anhydrous THF (15 mL) and methanol (100 mL). Triethylamine (10 drops) was added to the mixture, and the vessel was flushed with nitrogen. Palladium/charcoal (10%; 50 mg) was added to the mixture, and the reaction vessel was shaken under an atmosphere of hydrogen at 45 psi overnight. The catalyst was filtered off and the solvent removed under reduced pressure. Residual traces of triethylamine were removed under high vacuum. The crude dipyrrylmethane was taken up in dichloromethane (22 mL) and methanol (0.75 mL). *p*-Toluenesulfonic acid (200 mg) in methanol (0.75 mL) was added, and the mixture was stirred in the dark at room-temperature overnight. A saturated solution of zinc acetate in methanol (3.5 mL) was added and the mixture stirred for an additional 24 h. The solvent was then evaporated under reduced pressure and the residue dissolved in a small amount of TFA. The solution was diluted with 25 mL of dichloromethane and washed with water (15 mL), 5% $NaHCO_3$ solution (15 mL), and water (15 mL). Recrystallization from chloroform/methanol gave the diphenanthroporphyrin (19 mg; 27%) as purple crystals, mp > 300 °C; UV-vis (1% TFA−CH_2Cl_2): λ_{max} (log ϵ) 436 (5.11), 458 (5.14), 581 (4.12), 638 (4.60) nm; ^{1}H NMR (TFA−$CDCl_3$): δ −2.91 (2H, br s), −1.39 (2H, br s), 1.69 (6H, t, J = 6.7 Hz), 3.61 (6H, s), 4.10 (4H, q, J = 6.7 Hz), 8.17 (4H, m), 8.35 (4H, m), 9.26 (4H, d, J = 6.8 Hz), 9.91 (4H, m), 11.32 (4H, s); HR MS (FAB): calcd for $C_{50}H_{38}N_4$ + H: *m*/*z* 695.3166; found: 695.3165.

7,17-Bis(2-(methoxycarbonyl)ethyl)-8,18-dimethyldiphenanthro[9,10-*b*:9,10-*l*] porphyrin (27b). The title porphyrin was prepared by the procedure given for **27a** from benzyl 3-((5-formyl-3-(2-(methoxycarbonyl)ethyl)-4-methyl-2-pyrrolyl)methyl)phenanthro[9,10-*c*]pyrrole-1-carboxylate (96 mg). Following the demetalation step, the crude product was reesterified with 5% H_2SO_4−methanol at room-temperature overnight. The porphyrin was purified by chromatography on grade 3 alumina, eluting with dichloromethane. Recrystallization from chloroform/methanol gave the diphenanthroporphyrin (22 mg; 31%) as purple crystals, mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 428 (5.24), 568 (4.57), 591 (4.37), 645 (3.63) nm; UV-vis (1% TFA−CH_2Cl_2): λ_{max} (log ϵ) 438 (5.12), 459 (5.12), 583 (4.20), 635 (4.57) nm; ^{1}H NMR (TFA−$CDCl_3$): δ −2.98 (2H, br s), −1.39 (2H, br s), 3.14 (4H, t, J = 7.4 Hz), 3.63 (6H, s), 3.70 (6H, s), 4.40 (4H, t, J = 7.4 Hz), 8.19 (4H, t, J = 8.3 Hz), 8.34 (4H, q, J = 8.3 Hz), 9.28 (4H, d, J = 8.3 Hz), 9.89 (2H, d, J = 8.3 Hz), 10.05 (2H, d, J = 8.3 Hz), 11.33 (2H, s), 11.51 (2H, s); HR MS (FAB): calcd for $C_{54}H_{42}N_4O_4$ + H: *m*/*z* 811.3274; found: 811.3271. Dibutyl ester: purple crystals (chloroform−methanol), mp 282 °C; UV-vis ($CHCl_3$): λ_{max} (log ϵ) 409 (infl; 5.07), 429 (5.30), 550 (infl; 4.04), 573 (4.69), 591 (4.10), 647 nm (3.12). Zinc complex: green flakes (chloroform−methanol), mp > 300 °C; UV-vis ($CHCl_3$): λ_{max} (log ϵ) 440 (5.49), 565 (4.08), 614 nm (4.76).

13,17-Dibutyl-12,18-dimethyldiphenanthro[9,10-*b*:9,10-*g*]porphyrin (30). Diethyl 1,1′-diphenanthro[9,10-*c*]pyrrolylmethane-3,3′-dicarboxylate (**31a**; 294 mg) and potassium hydroxide (300 mg) were dissolved in ethylene glycol (30 mL). Nitrogen was allowed to bubble through the mixture for 5−10 min before placing the reaction flask in a preheated oil bath (190−200 °C). The mixture was heated under reflux under an atmosphere of nitrogen for 25 min. The reaction mixture was cooled and diluted with chloroform, washed with water (25 mL), and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue taken up in 550 mL of dichloromethane and 25 mL of methanol. Dialdehyde **22b**[1] (160 mg) and *p*-toluenesulfonic acid (596 mg) in methanol (25 mL) were added to the mixture, and the solution was stirred in the dark at room temperature overnight. A saturated solution of zinc acetate in methanol (20 mL) was added to the mixture and stirring was continued overnight. The mixture was washed with water, the solvent evaporated under reduced pressure, and the residue dissolved in a small amount of TFA to demetalate the zinc chelate and diluted with dichloromethane, washed with water, 5% aqueous sodium bicarbonate solution, and water. The solvent was evaporated under reduced pressure and the residue chromatographed on grade 3 alumina eluting initially with dichloromethane and then chloroform. The deep olive-green solutions were recolumned on grade 3 alumina, eluting initially with toluene. After a porphyrin byproduct had eluted, the eluent was switched to 5% ethyl acetate/toluene and an olive-green band was collected. Recrystallization from chloroform/methanol gave the diphenanthroporphyrin (65 mg; 18%) as a dark maroon powder, mp > 300 °C; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) 434 (5.26), 538 (4.15), 571 (4.46), 593 (4.08), 651 (4.16) nm; UV-vis (1% TFA-CH_2Cl_2): λ_{max} (log ϵ) 448 (5.27), 583 (4.32), 632 (4.50) nm; ^{1}H NMR (TFA-$CDCl_3$): δ −2.57 (2H, br s), −2.16 (2H, br s), 1.08 (6H, t, J = 7.3 Hz), 1.67 (4H, sextet), 2.11 (4H, pentet), 3.65 (6H, s), 4.04 (4H, t, J = 7.6 Hz), 8.13−8.26 (6H, m), 8.33 (2H, t), 9.27 (4H, d, J = 8.1 Hz), 9.73 (2H, d, J = 8.1 Hz), 9.96 (2H, d, J = 8.1 Hz), 10.47 (1H, s), 11.39 (2H, s), 12.32 (1H, s); ^{13}C NMR (TFA−$CDCl_3$): δ 12.0, 13.7, 23.1, 26.6, 34.2, 98.2, 100.1, 102.1, 125.3, 127.3 (2), 127.5, 127.8, 129.6, 129.8, 129.9, 130.4, 133.7, 133.9, 138.5, 138.6, 143.3, 143.5; HR MS (FAB): Calcd for $C_{54}H_{46}N_4$ + H: *m*/*z* 751.3790. Found: 751.3813. Nickel(II) complex: dark green powder (chloroform−methanol), mp > 300 °C; UV-vis ($CHCl_3$): λ_{max} (log ϵ) 429 (5.19), 551 (4.03), 594 (4.62) nm. Copper(II) complex: green crystals (chloroform−methanol), mp > 300 °C; UV-vis (5% pyrrolidine-$CHCl_3$): λ_{max} (relative ratios) 432 (1), 557 (0.064), 599 nm (0.198). Zinc complex: bright green crystals (chloroform−methanol), mp > 300 °C; UV-vis (trace pyrrolidine−$CHCl_3$): λ_{max} (log ϵ) 428 (4.27), 453 (5.02), 573 (3.86), 614 (4.12) nm.

Tetraphenanthro[9,10-*b*:9,10-*g*:9,10-*l*:9,10-*q*]porphyrin (10). A solution of ethyl phenanthro[9,10-*c*]pyrrole-1-carboxylate (500 mg) in THF (50 mL) was added dropwise over a period of 20−30 min to a stirred mixture of lithium aluminum hydride (130 mg) in THF (50 mL), maintaining the temperature of the mixture at 0 °C with the aid of a salt/ice bath. The mixture was stirred for an additional 1 h, water was added, and the organic phase was separated. The aqueous layer was extracted with chloroform (2 × 50 mL), and the combined organic solutions were washed with water (50 mL) and dried over sodium sulfate. The solvent was evaporated under reduced pressure, maintaining the temperature of the water bath at 25−30 °C. The residual oil was taken up in chloroform (125 mL), the air was purged with nitrogen, and 60 μL of a 2.5 M boron trifluoride etherate solution in dichloromethane was added. The resulting pale blue mixture was stirred in the dark at room temperature for 1 h. DDQ (290 mg) was added in a single portion, and stirring was continued for an additional 1 h. The mixture was washed with water (50 mL), 5% $NaHCO_3$ solution (50 mL), and water (50 mL), and the solvent was evaporated under reduced pressure. Recrystallization twice from chloroform/methanol gave the tetraphenanthroporphyrin (52 mg; 13%) as a dark green powder, mp > 400 °C; UV-vis (1%TFA−$CHCl_3$): λ_{max} (log ϵ) 482 (5.35), 615 (4.26), 668 (4.63) nm; ^{1}H NMR (TFA−$CDCl_3$): δ − 0.55 (4H, br s), 8.13 (8H, t), 8.24 (8H, t), 9.24 (8H, d, 8.3 Hz), 9.71 (8H, d, J = 8.2 Hz), 12.01 (4H, s); ^{13}C NMR (TFA−$CDCl_3$): δ 101.4 (*meso*-CH), 125.1, 126.9, 127.3, 129.6, 129.7, 129.8, 133.8, 139.5; HRMS (FAB): calculated for $C_{68}H_{38}N_4$ + H: *m*/*z* 911.3175; found: 911.3168. Anal. Calcd for $C_{68}H_{36}N_4 \cdot 2H_2O$: C, 86.23; H, 4.47; N, 5.92. Found: C, 86.15; H, 4.42; N, 5.93.

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Supporting Information Available: Copies of UV-vis spectra for porphyrins **10**, **19**, **20**, **27** and **30**, and ^{1}H and ^{13}C NMR spectra for compounds **10**, **12**, **14**, **16**, **17**, **19**, **20**, **27**, **28**, **30**, and **31** (54 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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